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⑩ **CANADIAN PATENT**

⑤④ PROCESS FOR THE PRODUCTION OF GAS MIXTURES FOR THE  
SYNTHESIS OF AMMONIA AND METHANOL, BY MEANS OF  
HIGH PRESSURE STEAM REFORMING OF GASEOUS AND  
LIQUID HYDROCARBONS

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No. OF CLAIMS 6

In the conventional processes known as "steam reforming", a hydrocarbon, e.g. methane, reacts with steam on a special catalyst according to:

$$\text{CH}_4 + \text{H}_2\text{O} \longrightarrow \text{CO} + 3\text{H}_2$$

The reaction is strongly endothermic with the heat required being supplied from the outside. The catalyst is contained in tubes of special steel capable of resisting high temperatures, arranged along the walls of a furnace wherein the complete combustion of part of the hydrocarbon with air takes place at atmospheric pressure. Conventionally, the maximum temperature attainable in the tubes is about 800-850°C and the maximum working pressure 25-30 kg/cm<sup>2</sup>. It is not possible in practice to exceed these values because of the mechanical strength of the tubes.

When a gas mixture is to be produced for the synthesis of NH<sub>3</sub>, the steam reforming is followed by a catalytic partial combustion with air, the amount of air being admitted is such that the proper ratio (H<sub>2</sub>+CO)/N<sub>2</sub> appears in the resulting gas.

The present invention improves the steam reforming process by adopting a process which is different from the above-described known process, making it possible to transform the hydrocarbons into H<sub>2</sub>+CO at very high pressures, even equal to those pressures required for synthesis of ammonia and of methanol.

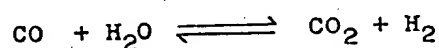
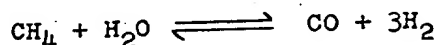
This new process forming the subject matter of my invention makes possible achieving advantages both in the operating cost and the plant cost, as compared with the conventional processes of steam reforming.

Figs. 1, 2 and 3 of the appended drawings illustrate three embodiments of the steam reforming process at high pressure, according to this invention.

The process methane, suitably compressed and preheated in preheater F1 is mixed with steam and enters the reformer H1 (Fig. 1). A part of the fumes generated, outside the tubes, by the complete combustion of part of the methane, is mixed with the



1 methane and steam mixture. The amount of fumes added to the methane is such as to ensure the desired  $H_2/N_2$  ratio in the gas transformed. The gas entering the catalyst carrying tubes consists therefore of a mixture of  $CH_4$ ,  $H_2O$ ,  $CO_2$ ,  $N_2$ , A. This gas flows on the catalyst and the methane present is transformed into  $H_2 + CO + CO_2$  by the reactions:



10 Because of heat supplied from the outside, the gas reaches a temperature of about  $1000^\circ C$ . This corresponds to a very low content of residual  $CH_4$ . The gas so produced passes onto the return tubes (contained in the catalyst carrying tubes) where it yields part of its sensible heat to the gas in the reforming stage. The remaining part of the heat required for the process is supplied by the complete combustion of a part of the methane with air at the same pressure at which the reforming is performed. This combustion may be effected in the very body containing the catalyst-carrying tubes, as in the present case, or in a separate gas generator. The combustion temperature is controlled by recycling a part of the comparatively cold fumes coming from the reformer, by means of an injector in which the injecting fluid is the air supporting the combustion. The part of fumes to be evacuated, after reduction of the temperature in a special exchanger, is expanded down to atmospheric pressure in a gas turbine connected to the air turbocompressor, thus achieving a considerable recovery of energy. The steam required for the process is produced by utilizing the thermal content of the transformed gas.

The characteristic features of the process are as follows:

30 The reforming takes place at equilibrium pressure. This permits, independently from the working pressure, very high temperatures in the catalyst-carrying tubes and, therefore, extremely high degrees of methane conversion.

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Nitrogen is introduced directly into the methane prior to reforming. Hence, it is unnecessary to carry out an after-combustion as in the conventional steam reforming process.

Excess fumes of the nitrogen required are expanded in a turbine thereby recovering a good deal of the energy necessary for the compression of air.

The combustion temperature is controlled by recycling part of the fumes. This is done by an injector or other means.

10 My process is particularly suitable to reform liquid and gaseous hydrocarbons in a pressure range which is considerably greater than that of conventional reformers. The best application range is from 50 to 250 abs. atm., preferably 150 abs.atm. It is best to use very high output capacities in order to realize the energy recovery on which the process is based.

The following example is to illustrate and not to limit the present invention.

The data of the new process hereinbelow sets the output capacity at about 800 tons/day of  $\text{NH}_3$  and the working pressure of the reformer at 150 abs.atm.

20 In Fig. 1, the methane starting material is compressed to about 160 abs.atm. and subsequently preheated up to about  $550^\circ\text{C}$  in a special small furnace F1. The preheated methane is divided into two parts. The first part consisting of  $22,250 \text{ Nm}^3/\text{hr}$  is mixed with  $193,050 \text{ Nm}^3/\text{hr}$  of steam superheated at 150 abs.atm. and introduced into the top of reformer H1. The remaining part, namely  $8,070 \text{ Nm}^3/\text{hr}$ , is completely burnt with air at the outside of the catalyst-carrying tubes of the reformer. The methane and steam entering the reformer at  $550^\circ\text{C}$ , are mixed with  $34,700 \text{ Nm}^3/\text{hr}$  of fumes coming, at the temperature of  $625^\circ\text{C}$ , from the zone out-  
30 side the catalyst-carrying tubes.

The composition of these fumes is:

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1	CO <sub>2</sub>	9.50 vol. %
	N <sub>2</sub> +A	71.50 " "
	H <sub>2</sub> O	19.00 " "
		<hr/> 100.00 vol. %

The two gas streams mix together, attaining a temperature of 567°C, and enter the catalyst-carrying tubes where, because of the heat supplied from the outside, the reforming reaction takes place. The transformed gas produced, leaves the catalyst bed at the temperature of 1,025°C and is cooled down to 700°C in the return tubes. Boiler F2 at 160 abs.atm. produces steam.

The characteristics of the transformed gas are:

flow rate (on the dry substance)	125,000 Nm <sup>3</sup> /hr
steam content	134,900 kg/hr
composition (on the dry substance):	

	CO	8.83 vol. %
	CO <sub>2</sub>	10.90 " "
	H <sub>2</sub>	59.49 " "
	CH <sub>4</sub>	0.71 " "
20	N <sub>2</sub>	19.82 " "
	A	0.25
		<hr/> 100.00 vol. %

The flow rate of the combustion air is 77,000 Nm<sup>3</sup>/hr; this air is compressed up to 160-170 abs. atm. by the centrifugal compressor CR. This air is preheated up to 550°C in a special small furnace F3 and, prior to entering the reformer, recycles by means of the injector EJ<sub>1</sub> about 125,000 Nm<sup>3</sup>/hr of fumes.

The combustion temperature is 1,400°C. The overall flow rate of fumes flowing at the outside of the catalyst-carrying tubes is about 210,000 Nm<sup>3</sup>/hr. The fumes are cooled from 1,400°C down to 625°C thereby supplying the heat required for the reforming. The fumes to be evacuated from the cycle (about 50,000 Nm<sup>3</sup>/hr)

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1 after having been cooled down to 550°C in heat exchanger F<sup>4</sup> are expanded in the turbine T<sub>1</sub>, thereby allowing to recover a 52% of the compression energy of the combustion air. Additional steam is expanded in turbine T<sub>2</sub> to make up the energy required for compressor TR<sub>1</sub>.

10 The variation of the invention shown in Fig. 2 controls the combustion temperature in the reformer (or in the gas producer generating the fumes) is effected by steam injection only, in lieu of recycling the fumes by means of injectors. Obviously, the fumes to be evacuated will have a steam content higher than in the case of Fig. 1. Consequently, the energy recovered in the turbine will be greater.

20 The variation shown in Fig. 3, also relates to the control of the combustion in the lower part of the reformer. The combustion temperature is still adjusted by steam as in Fig. 2, but a great part of the steam is introduced into the cycle, while humidifying the air in humidification column C<sub>1</sub> and condensation column C<sub>2</sub> at the expense of the heat of that part of fumes that is to be evacuated from the cycle.

30 Meaning and figures in which the symbols appear are:

		FIGS.
CR <sub>1</sub>	- air turbocompressor	1, 2, 3
F <sub>1</sub>	- methane preheater	1, 2, 3
F <sub>2</sub>	- boiler at 160 abs.atm.	1, 2, 3
F <sub>3</sub>	- air preheater	1, 2, 3
F <sub>4</sub>	- heat exchanger	1, 2, 3
H <sub>1</sub>	- reformer at equilibrated pressure	1, 2, 3
T <sub>1</sub>	- gas turbine	1, 2, 3
T <sub>2</sub>	- steam turbine	1, 3
C <sub>1</sub>	- air humidification column	3
C <sub>2</sub>	- condensation column	3
PC <sub>1</sub>	- centrifugal pump	3

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In the steam reforming process for the production of a synthesis gas of carbon monoxide and hydrogen from gaseous and liquid hydrocarbons wherein nitrogen is introduced into the hydrocarbon in the presence of a reforming catalyst, the improvement which comprises carrying out the steam reforming in tubes or pipes containing a catalyst, said tubes or pipes being spaced apart in a reactor, the pressure within the tubes or pipes being equal to the pressure outside said tubes or pipes and being at a value between 50 and 250 abs. atm.
2. The process of claim 1, wherein methane is the hydrocarbon and the pressure is at 160 abs. atm.
3. The process of claim 2, wherein nitrogen is introduced into the methane prior to steam reforming.
4. The process of claim 3, wherein a combustion of the hydrocarbon with air takes place outside the steam reforming process per se, said combustion producing fumes, and using energy obtained from expanding said fumes to compress the combustion air.
5. The process of claim 4, wherein part of the fumes is recycled to the combustion, thereby controlling combustion temperature.
6. The process of claim 4, wherein the combustion temperature is controlled by steam injection.



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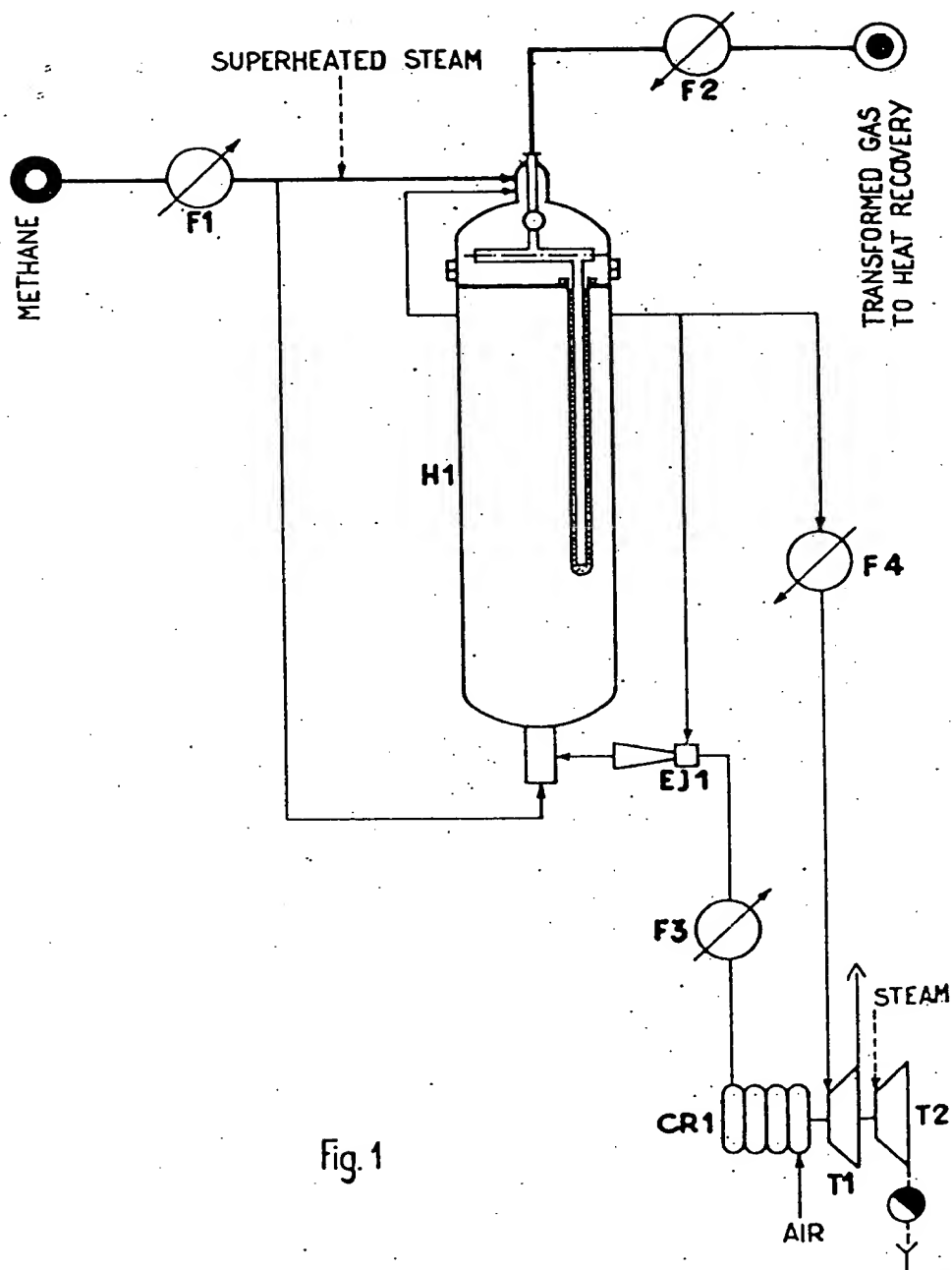


Fig. 1

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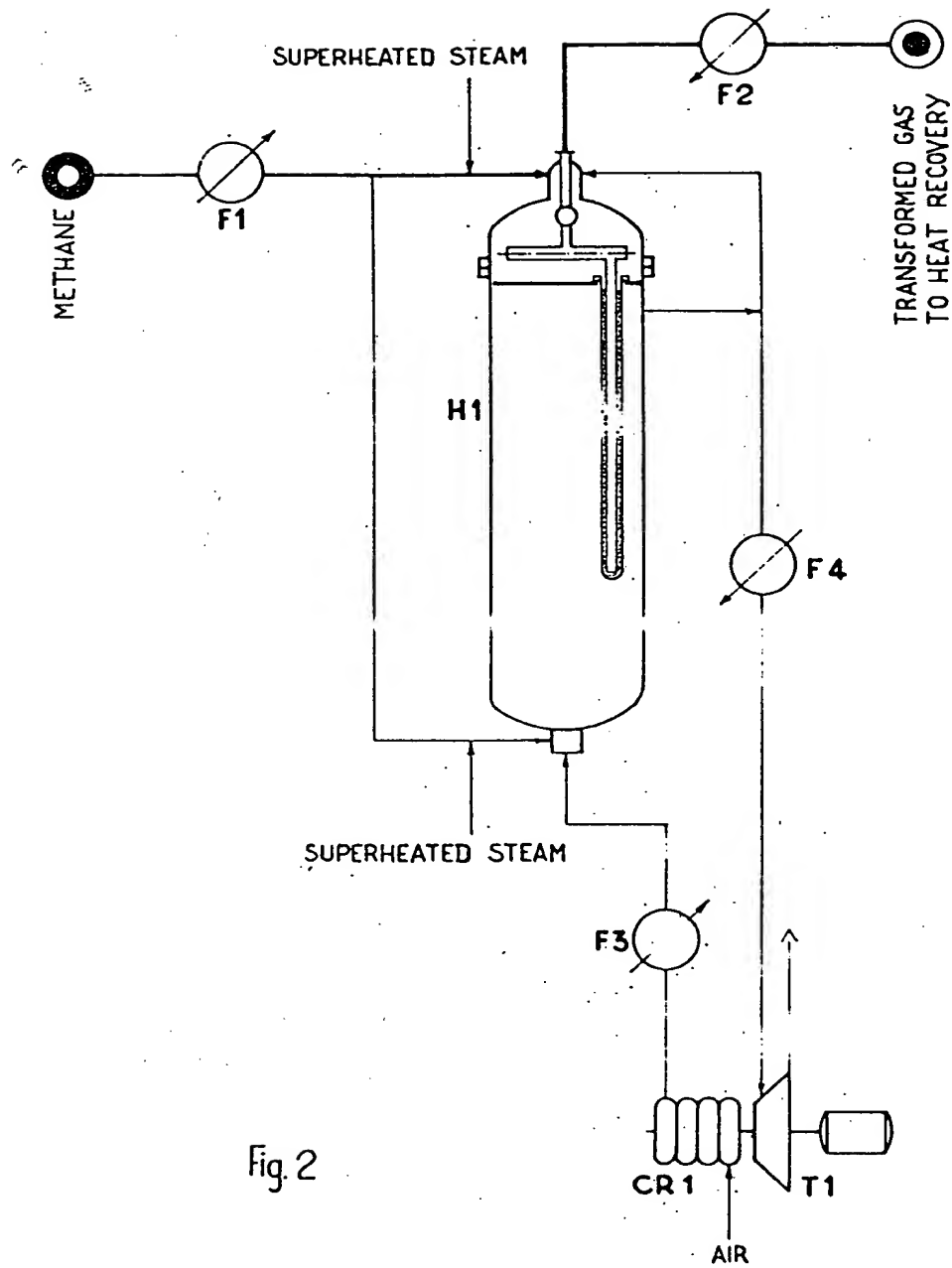


Fig. 2

